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(54) Title: LOW SINTERING TEMPERATURES CONDUCTIVE NANO-INKS AND A METHOD FOR PRODUCING THE SAME

(57) Abstract: The present invention discloses a novel and cost effective method for the production of conductive inks comprising metal nano-powders. The method comprising the four steps of (i) admixing metal nano powder in a solvent with at least one ingredient of the group selected from: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; (ii) applying the homogenized mixture obtained above on a surface to be coated; (iii) evaporating the solvent from said homogenized mixture; and lastly (iv) sintering the coated layer at temperature range of 50°C to 300°C, providing a conductive ink on top of said surface characterized by resistances between 0.005 Ω/square to 5 Ω/square. The present invention also discloses conductive ink comprising metal nano-powders obtained by a process comprising *inter alia* the step of low temperature sintering at ambient pressure.



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LOW SINTERING TEMPERATURES CONDUCTIVE NANO-INKS AND A METHOD FOR PRODUCING THE SAME

FIELD OF THE INVENTION

The present invention relates to low sintering temperatures conductive nano-inks and to a method for producing the same.

BACKGROUND OF THE INVNETION

Metal nano-powder materials are single phase or multi-phase polycrystals, with particle size in the order of a few nanometers (typically 1-100) in at least one dimension. It is well acknowledged that wherein conventional polycrystalline materials grain boundaries account for less than 1% of the volume, in nano structured materials can occupy as much as 50%. Nano particles, specially metal nano particles have hence very special properties which are directly related to their dimensions and to the fact that a large ratio of the atoms in the particle are in the surface of the particle or at particle and grain boundaries. These properties include optical properties, diffusion properties, electrical properties like capacitance, impedance and resistance, catalytic activity and many others.

These improved properties have a range of uses and applications; e.g. catalysts for chemical reactions, electrodes, fuel cells, medical devices, water cleaning technologies, electronic devices, coatings and more.

Nano-inks and nano-powders for coatings characterized by a significant electrical conductivity are useful, but not exclusively, for printing of electrical connections in circuits such as, antennas, smart tags, display panels, printed circuit boards, chips and others.

Literature presents few hints regarding the sintering step of nano-particles. Most of the art suggests sintering at respectively high temperature ranges. Hence, U.S. Pat. No. 6,582,651 to Cochran, Jr. *et al.* discloses a process for forming a shaped metallic article, comprising *inter alia* the steps of (i) combining starting materials, the starting

materials comprising a nonmetallic metal precursor nano-powder; (ii) forming the starting materials into a free standing, unsupported shape to produce a nonmetallic article of a certain geometry; (iii) chemically converting the nonmetallic article to a metallic article with a reducing agent while substantially retaining the geometry of the nonmetallic article; and (iv) sintering the metallic article at 500°C to 1,450°C to form a more dense metallic article while substantially retaining the geometry of the nonmetallic article. Similarly, U.S. Pat. No. 5,147,446 to Pechnik *et al.*, discloses a method for fabrication of dense compacts from nano-sized particles using high pressures and cryogenic temperatures, wherein the sintering step is applied in the temperature range of 1,000°C to 1,500°C.

U.S. Pat. No. 6,395,214 to Kear *et al.* discloses another approach and presents a method for fabricating a nano-crystalline ceramic article at respectively low temperature yet by applying very high pressures. Hence, their method comprises the steps of (i) synthesizing loosely-agglomerated ceramic nano-powder having a metastable structure; (ii) forming the ceramic nano-powder into a compact; and then (iii) sintering the ceramic nano-powder compact under a pressure of 3 GPa to 5.5 GPa and at a temperature no greater than about 0.6 times the melting temperature of the ceramic nano-powder to form the nano-crystalline article.

A useful and cost effective method for sintering nano-particles, and especially electrically conductive nano-ink powders at respectively low temperatures and at ambient pressure is thus a significant industrial need.

BRIEF DESCRIPTION OF THE INVENTION

In order to understand the invention and to see how it may be carried out in practice preferred embodiments will now be described, by way of non-limiting example only, with reference to the accompanying figures, in which:

Fig. 1: The change of relative resistance for silver nano powders coated with surfactant (1) and washed from surfactant (2);

Fig. 2: Relative resistance dependence on temperature for the different particle size silver powders – and measured bulk silver in our measuring system; and

Fig. 3: Relative resistance dependence on temperature for the different particle size copper powders – and measured bulk copper in our measuring system.

SUMMARY OF THE INVENTION

It is the main purpose of the present invention to provide useful and novel method for the production of conductive inks comprising metal nano-powders. Said method comprising *inter alia* the following four steps: (i) admixing metal nano powder in a solvent with at least one ingredient of the group selected from: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; (ii) applying the homogenized mixture obtained above on a surface to be coated; (iii) evaporating the solvent from said homogenized mixture; and lastly and most importantly, (iv) sintering the coated layer at temperature range of 50°C to 350°C, providing a conductive ink on top of said surface characterized by resistances between 0.005 Ω /square to 5 Ω /square. Said sintering is preferably provided at ambient pressure (e.g., about atmospheric pressure).

It is in the scope of the present invention wherein the sintering step is provided at temperature of about 50°C. Alternatively or additionally, it is in the scope of the present invention wherein the sintering step is provided for 0.5 to 2 hours.

The present invention also relates to the aforementioned method, wherein the metal nano powder is selected from at least one of the group: metal nano powder; metal nano powder with metal colloids; metal nano powder with a metal reducible salt and/or organic metal complexes and/or organo-metal compounds which decompose to form conductive materials. The concentration of the metal nano-powder in the admixed solution may be between 1% (wt) to 70% (wt). More specifically, the concentration of the metal nano powder in the admixed solution may be between 2% (wt) to 50% (wt).

The admixed solution comprising organic solvent or a mixture of organic solvents including UV and thermally curable monomers. Moreover, the concentration of the organic solvent or the mixture of organic solvents in the admixed solution is between 20% (wt) to 85% (wt). Most specifically, said range is between 40% (wt) to 80% (wt).

The aforementioned solvent is preferably selected from at least one of the group of petroleum ether, hexane, heptanes, toluene, benzene, acrylates, dichloroethane, trichloroethylene, chloroform, dichloromethane, nitromethane, dibromomethane, cyclopentanone, cyclohexanone or any mixture thereof. The concentration of the aforementioned binder in the admixed solution is preferably between 0% (wt) to 5% (wt). Said binder may be selected from ethyl cellulose and/or modified urea.

It is further in the scope of the present invention wherein the surface to be coated is selected from ceramics, glass, either flexible or relatively non-flexible polymeric films or sheets, polyimides, kepton, polyethylene products, polypropylene, acrylate containing products, polymethyl metaacrylate, e.g., PMMA or Perspex, their co-polymers or any combination thereof, or any printable substrate.

More specifically, the polymeric film comprising at least one of the group of polyesters, polyamides, polycarbonates, polyethylene, polypropylene, their copolymers or any combination thereof.

It is also in the scope of the present invention wherein the method is additionally comprises of a step of treating the surface to be coated by a means of corona treatment and/or coating by primer. Such a primer may be selected from at least one of the group of 3-aminopropyl triethoxy silane, phenyl trimethoxysilane, glycidyl trimethoxysilane, commercially available Tween products, Tween-80, neoalkoxy tri(dioctylpropylphosphato) titanate or any combination thereof.

It is also in the scope of the present invention wherein the nano-powder comprising metal or a mixture of metals selected from silver, gold, platinum, palladium, nickel, cobalt, copper or any combination thereof or any other conductive metal. Additionally or alternatively, said metal is admixed with metal colloids; metal nano powder with a metal reducible salt and/or organic metal complexes and/or organo-metal compounds which decompose to form conductive materials.

The aforementioned method may comprise the step of polymerizing a monomer in the presence of catalyst and/or oxidizing agent and/or reducing agent, in the manner a

water miscible polymer is obtained in the homogenized solution. The spreading of the homogenized mixture on a surface to be coated may be provided by a means selected from simple spreading; bar spreading, immersing; spin coating; doping and/or dipping. Moreover, the coating layer or layers provided by the spreading of the homogenized mixture on a surface to be coated may be characterized by a wet thickness of 1 to 200 microns.

It is still another object of the present invention to provide useful any conductive ink comprising metal nano-powders obtained by a process comprising *inter alia* the step of low temperature sintering at ambient pressure.

It is still in the scope of the present invention to provide the conductive nano-ink as defined above, printed or coated in a predetermined pattern, and to provide a self assembled conductive nano-ink. Particularly, it is in the scope of the present invention to provide the conductive nano-ink, especially adapted for post treatment of surface; wherein said treatment is selected from scratch resistance, increasing adhesion or a combination thereof.

It is a final object of the present invention to provide useful any conductive ink (e.g., nano-powders characterized by resistances between 0.005 Ω /square to 5 Ω /square) comprising metal nano-powders obtained by the method defined in any of the above.

DETAILED DESCRIPTION OF THE INVENTION

The following description is provided, along all chapters of the present invention, so as to enable any person skilled in the art to make use of said invention and sets forth the best modes contemplated by the inventor of carrying out this invention. Various modifications, however, will remain apparent to those skilled in the art, since the generic principles of the present invention have been defined specifically for low sintering temperatures conductive nano-inks and to a method for producing the same.

A novel method of low temperature sintering useful for the production of conductive coatings and inks comprising metal nano-powders (i.e., coatings or inks) is hereby presented. It is according to the present invention that by coating a substrate with an ink, solution or paste that was previously dispersed, cost-effective nano conductive materials and/or conductive transparent coating are produced.

The term 'coating' is referring according to the present invention to any conductive layer produced in the manner of admixing metal nano powder in a solvent with at least one ingredient of the group: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; and then sintering at respectively low temperatures of 50 to 300°C.

The term 'ink' is referring according to the present invention to any ink containing nano-powders of metal or metals, especially emulsion based compositions provided for coloring materials, or alternatively, to legend ink (marking ink) suitable for printing on printed circuit boards (PCB's).

More specifically, the term 'ink' is referring according to the present invention to any conductive topical pattern produced in the manner of admixing metal nano powder in a solvent with at least one ingredient of the group: binder, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; the solution can be admixed, but not essential, with water or water miscible solvent or mixture of water miscible solvents in the manner a W/O type emulsion is obtained; spreading or printing the homogenized mixture obtained above on said surface to be coated; evaporating the solvent from said homogenized mixture in the manner that a self-assembled network-like pattern is developed *in situ* or a printed pattern or a

complete coverage is formed; and then sintering the network-like pattern at respectively low temperatures of 50 to 300°C so a conductive and nano-ink is obtained.

The inks (e.g., ink paste, inks, solutions, coatings) according to the present invention can also especially be adapted for use in or on top of transparent substrates. The aforementioned ink is adapted for coating, covering, immersing, dipping, and/or entrapping on top or into either solid or semi-solid matrix, or by means of any other suitable technique on such as glass or any polymer matrix, including flexible, semi-flexible or rigid materials.

The present invention discloses the novel properties of the nano metal powders and inks (i.e., conductive-polymers, as well as conductive metals, oxides characterized by $D_{50} < 60\text{nm}$ and $D_{90} < 100\text{nm}$). Those properties enable the hereto-defined nano-powders to provide an industrial scale production of flexible electrical circuits on substrates such as polymer films and plastics.

It is according to one embodiment of the present invention to provide nano sized particles and grains that have much larger surface area than bulk materials, characterized by special diffusion properties and can be processed so continuous conductive phase is produced at relative low temperatures and lower energy input.

It is according to another embodiment of the present invention to coat a substrate with a nano metal powder or ink. Alternatively, it is according to another embodiment of the present invention to coat a substrate with a solution or paste, in which the nano metal powder were dispersed and sintered at low temperatures of about 50°C and preferably around 100°C to 220°C, in the manner conductive layers characterized by resistances between 0.005 Ω/square to 5 Ω/square are obtained

These resistance values are comparable to resistivity values of between $2.1 \cdot 10^{-5}$ and $6.6 \cdot 10^{-4} \Omega \cdot \text{cm}$. The lowest resistivity obtained is about only 1.5 times higher than bulk silver as measured in our system. While commercially available and literature cited technologies suggested to produce conductive layers require sintering temperatures over 300°C and usually near 900°C the present invention discloses a novel method of

sintering at temperatures lower 250°C and/or lower the Tg or melting point of flexible materials such as plastics and polymers.

It is according to another embodiment of the present invention to provide useful printing techniques, selected from screen-printing, manual applicator and manual spreading, lithography, ink jet printing, screen printing, offset printing, fill and mill dispensing machine, spin coating and spray coating yet not limited to them.

Hence, according to yet another embodiment of the present invention almost any type of substrates can be coated. More particularly, those substrates are selected, yet no limited to glass, poly-carbonate, polymer films or any combination thereof.

Examples for formulations for each method are described bellow. These are only representative examples and are described hereby to demonstrate the wide range of possibilities this invention covers, by which we can use the special properties of nano metal powders. It is further acknowledged that the formulations of the hereto-described examples may similarly be made with different binders, solvents, metal powders, additives, polymers, buffers, surfactants, dispersants and/or coupling agents. Nevertheless, according to the present invention, nano powder metals and/or nano powder metal salts characterized by small particle size ($D_{90} < 0.1 \mu\text{m}$) which are conductive are especially preferred. Concentrations can be adjusted to control the viscosity and the resistance and transparency of the coated substrate.

It is the scope of the present invention wherein the Resistance is calculated by Ohms law, $V = I * R$; wherein the Resistivity - ρ equals $R \cdot (H \cdot W / L)$, where H is the thickness of the powder layer, W is its width, and L is the length of the layer and further wherein Relative Resistance equals $(R_0 - R) / R_0$; R_0 is the initial resistance of the sample.

EXAMPLE 1

Dry nano Silver metal powders

Silver powders of different sizes, including nano size powders, were produced through the procedure described in U.S. Pat. No. 5,476,535, which is hereto provided as a reference. The powders are coated with organic materials and de-agglomerated. The

volume particle size distribution of these powders, measured in a Coulter Particle Size Analyzer LS 230, are presented in Table 1.

Table 1. Silver powders used in experiments

Sample Number	Particle Size Distribution	
	D ₅₀ μm	D ₉₀ μm
1	0.054	0.067
2	0.054	0.066
3	0.052	0.063
4	0.246	2.851
5	3.2	8

The electrical resistances of these powders were measured as a function of the sintering process, see Tab. 2 and Tab. 3.

Reference is made now to figure 1, presenting the change of relative resistance for silver nano powders coated with surfactant (1) and washed from surfactant (2). Reference is made now to figure 2, presenting the relative resistance dependence on temperature for the different particle size silver powders – and measured bulk silver in our measuring system.

Samples 1, 2 and 3 are nano silver powders; samples 4 and 5 are coarse silver powders with a particle size of over 2.5 μm (D₉₀). As can be seen nano silver powders achieve better conductivities at lower temperatures. A nano silver powder washed from its coating will give the same performance at even lower temperatures of about 100°C in comparison to around 220°C for the coated powder and over 700°C for coarse silver powders.

Table 2: Electrical properties of silver powders

Sample 1 (coated with surfactant)			Sample 2 (washed from surfactant)		
Resistance R, Ω	Resistivity ρ , $\Omega \cdot \text{cm}$	Temperature $^{\circ}\text{C}$	Resistance R, Ω	Resistivity ρ , $\Omega \cdot \text{cm}$	Temperature $^{\circ}\text{C}$
1300	7.60	236	0.1065	1.24E-3	62
131	0.76	270	0.0166	1.94E-4	127

Table 3: Electrical properties of different particle size silver powders at different sintering temperatures.

Sample Number	T = 120 $^{\circ}\text{C}$		T = 220 $^{\circ}\text{C}$	
	Resistance R, Ω	Resistivity ρ , $\Omega \cdot \text{cm}$	Resistance R, Ω	Resistivity ρ , $\Omega \cdot \text{cm}$
2	0.0203	2.40E-4	0.0034	3.98E-5
4	0.1600	1.20E-3	0.0860	6.61E-4
5	0.4620	3.24E-3	0.4200	2.95E-3
Bulk Silver*	0.0040	1.95E-5	0.0045	2.14E-5

* bulk silver measured under same conditions and set-up.

EXAMPLE 2

Dry nano Copper metal powders

Copper powders of different sizes, including nano size powders were produced through the procedure described in U.S. Pat. No. 5,476,535, which is hereto provided as a reference. The powders were coated with organic materials and de-agglomerated. The volume particle size distribution of these powders, measured in a Coulter Particle Size Analyzer LS 230, are presented in Table 4.

Table 4. Copper powders used in experiments

Sample Number	Particle Size Distribution		Surface area m^2/g
	D_{50} μm	Mean μm	
AS0873	0.073	0.181	7.2
ASX0871	0.35	0.317	6.0
ASX13-1	3.4	3.4	1.3

The electrical resistances of these powders were measured as a function of the sintering process. Reference is made hence to Fig. 3, presenting the relative resistance dependence on temperature for the different particle size copper powders – and measured bulk copper in our measuring system.

EXAMPLE 3

Nano metal powders in formulations.

The formulations are inks or pastes, which facilitate the printing and/or coating process, were prepared according to the general procedures described bellow. Care has to be taken to achieve a good dispersion of the conductive additives (metal nano powders, salts and/or colloids).

Three ink/paste systems were tested. All three have been found to produce a conductive coating at low sintering temperatures. The systems differ in the formulation concept, and main ingredients leading to the conductivity. The main ingredients of the systems are: 1) metal nano powder, 2) metal nano powder with metal colloids, 3) metal nano powder with a metal reducible salt.

Examples for formulations for each method are described bellow. Resistance results for these systems are presented in Tab. 5.

System 1 (described above) formulation; P0010

Admixing a binder (e.g., ethyl cellulose), 13% (wt/wt) in a solvent (e.g., terpinol). Then, admixing a conductive nano powder metal (e.g., silver nano powder) (D90 < 0.1 μm); 50 parts by weight; terpinol 20 parts by weight, and a coupling agent such as isopropyl dioleic(dioctylphosphato)titanate, also known as the commercially available NDZ-101 KRTTS, 1 parts by weight, to some 25 parts by weight of the solution obtained above, by a means of a high rpm homogenizer.

System 2 (described above) formulation; C121

Intensively admixing colloidal silver, 12 parts by weight; a binder e.g., a binder which is an adhesion promoter, such as Polyvinyl Pyrrolidone (PVP), 2.5 parts by weight; water, 32 parts by weight by a means of an ultrasonic energy and/or high rpm dispersing equipment.

Then, admixing a conductive nano powder metal (e.g., silver nano powder) ($D_{90} < 0.1 \mu\text{m}$), 14 parts by weight; solvent (e.g., ethanol), 39.5 parts by weight by a means of a high rpm homogenizer. Finally admixing the second mixture to the first mixture while mixing and stirring thoroughly.

System 3 (described above) formulation: Cl16

Admixing silver formate salt, 1 parts by weight; a dispersant, e.g., trioctylphosphine oxide (TOPO), 2 parts by weight; and a solvent (e.g., ethyl acetate), 80 parts by weight at about 60°C until all components dissolve. Then, admixing a conductive nano powder metal (e.g., silver nano powder) ($D_{90} < 0.1 \mu\text{m}$), 17 parts by weight to the obtained brown solution by a means of a high rpm homogenizer.

Table 5: Resistance data for nano metal powders ink formulations.

System	Formulation	Resistance Ω/square	Resistivity $\Omega \text{ cm}$	Sintering Temperature, $^\circ\text{C}$
1	P0010	0.7	2.84E-4	120
1	P0010	0.05	2.03E-5	300
3	Cl16	2.8	6.72E-5	120
3	Cl16	1.17	2.93E-5	300
2	Cl21	0.255	3.09E-4	100
	Bulk Silver*	0.004	1.95E-5	120
	Bulk Silver*	0.0045	2.14E-5	220

* Bulk silver measured under same conditions and set-up.

CLAIMS

1. A method for the production of conductive inks comprising metal nano-powders, said method comprising;
 - i. admixing metal nano powder in a solvent with at least one ingredient of the group selected from: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained;
 - ii. applying the homogenized mixture obtained above on a surface to be coated;
 - iii. evaporating the solvent from said homogenized mixture; and,
 - iv. sintering the coated layer at temperature range of 50°C to 300°C, providing a conductive ink on top of said surface characterized by resistances between 0.005 Ω /square to 5 Ω /square.
2. The method according to claim 1, wherein the sintering step is provided at temperature of about 50°C.
3. The method according to claims 1 or 2, wherein the sintering step is provided for 0.5 to 2 hours.
4. The method according to claim 1, wherein the metal nano powder is selected from at least one of the group: metal nano powder; metal nano powder with metal colloids; metal nano powder with a metal reducible salt and/or organic metal complexes and/or organo-metal compounds which decompose to form conductive materials.
5. The method according to claim 4, wherein the concentration of the metal nano powder in the admixed solution is between 1% (wt) to 70% (wt).
6. The method according to claim 4, wherein the concentration of the metal nano powder in the admixed solution is between 2% (wt) to 50% (wt).
7. The method according to claim 1, wherein the admixed solution comprising organic solvent or a mixture of organic solvents.

8. The method according to claim 1, wherein the admixed solution comprising organic solvent or a mixture of organic solvents, and UV and thermally curable monomers.
9. The method according to claim 1, wherein the concentration of the organic solvent or the mixture of organic solvents in the admixed solution is between 20% (wt) to 85% (wt).
10. The method according to claim 1, wherein the concentration of the organic solvent or the mixture of organic solvents in the admixed solution is between 40% (wt) to 80% (wt).
11. The method according to claim 1, wherein the solvent is selected from at least one of the group of petroleum ether, hexane, heptanes, acrylates, toluene, benzene, dichloroethane, trichloroethylene, chloroform, dichloromethane, nitromethane, dibromomethane, cyclopentanone, cyclohexanone or any mixture thereof
12. The method according to claim 1, wherein the concentration of the binder in the admixed solution is between 0% (wt) to 5% (wt).
13. The method according to claim 1, wherein the binder is selected from ethyl cellulose and/or modified urea.
14. The method according to claim 1, wherein the surface to be coated is selected from glass, either flexible or relatively non-flexible polymeric films or sheets, polyethylene products, polypropylene, acrylate containing products, PMMA, their co-polymers or any combination thereof.
15. The method according to claim 13, wherein the polymeric film comprising at least one of the group of polyesters, polyamides, polycarbonates, polyethylene, polypropylene, their copolymers or any combination thereof.
16. The method according to claim 1, additionally comprising the step of treating the surface to be coated by a means of corona treatment and/or coating by primer.

17. The method according to claim 15, wherein the primer is selected from at least one of the group of 3-aminopropyl triethoxy silane, phenyl trimethoxysilane, glycidyl trimethoxysilane, commercially available Tween products, Tween-80, neoalkoxy tri(dioctylpropylphosphato) titanate or any combination thereof.
18. The method according to claim 1 wherein the nano-powder comprising metal or a mixture of metals selected from silver, gold, platinum, palladium, nickel, cobalt, copper or any combination thereof.
19. The method according to claim 1 wherein the nano-powder comprising metal is admixed with metal colloids; metal nano powder with a metal reducible salt and/or organic metal complexes and/or organo-metal compounds which decompose to form conductive materials.
20. The method according to claim 1, comprising the step of polymerizing a monomer in the presence of catalyst and/or oxidizing agent and/or reducing agent, in the manner a water miscible polymer is obtained in the homogenized solution.
21. The method according to claim 1, wherein the spreading of the homogenized mixture on a surface to be coated is provided by a means selected from simple spreading; bar spreading, immersing; spin coating; doping and/or dipping.
22. The method according to claim 20, wherein the coating layer or layers provided by the spreading of the homogenized mixture on a surface to be coated is characterized by a wet thickness of 1 to 200 microns.
23. The method according to claim 1, wherein the sintering step is provided at ambient pressure.
24. The method according to claim 1, additionally comprising a step of washing the powder before sintering so a lower temperature is required for the onset of the conductivity.

25. Conductive nano-ink comprising metal nano-powders obtained by a process comprising *inter alia* the step of low temperature sintering at ambient pressure.
26. Conductive nano-ink comprising metal nano-powders obtained by the method defined in claims 1 to 24.
27. The conductive nano-ink according to claim 25, printed or coated in a predetermined pattern.
28. A self assembled conductive nano-ink according to claim 25.
29. The conductive nano-ink according to claim 25, especially adapted for post treatment of surface; wherein said treatment is selected from scratch resistance, increasing adhesion or a combination thereof.

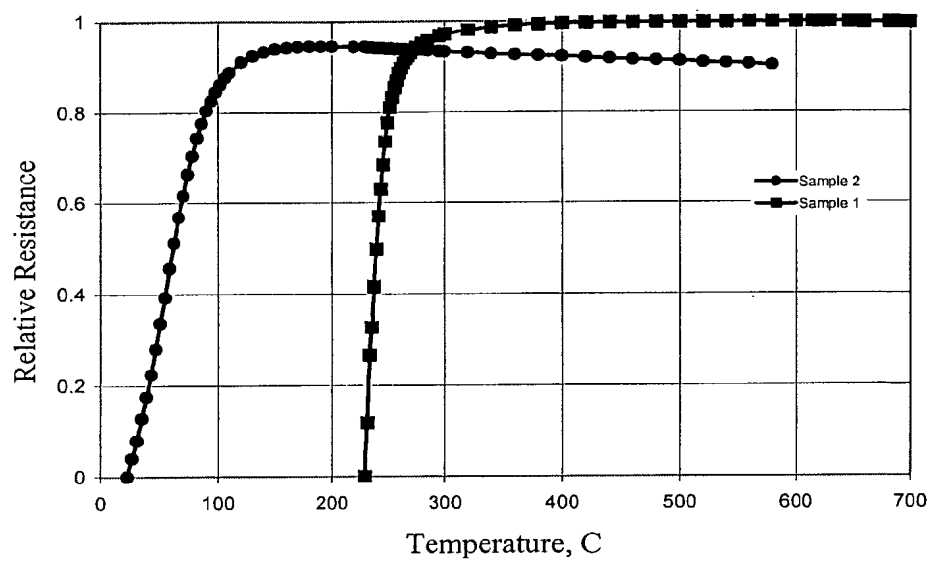


Figure 1

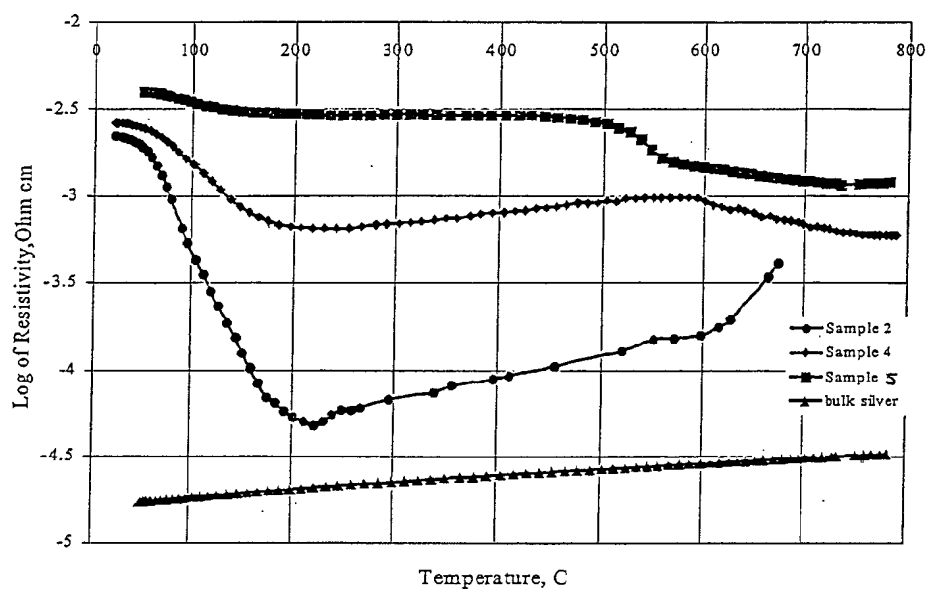


Figure 2

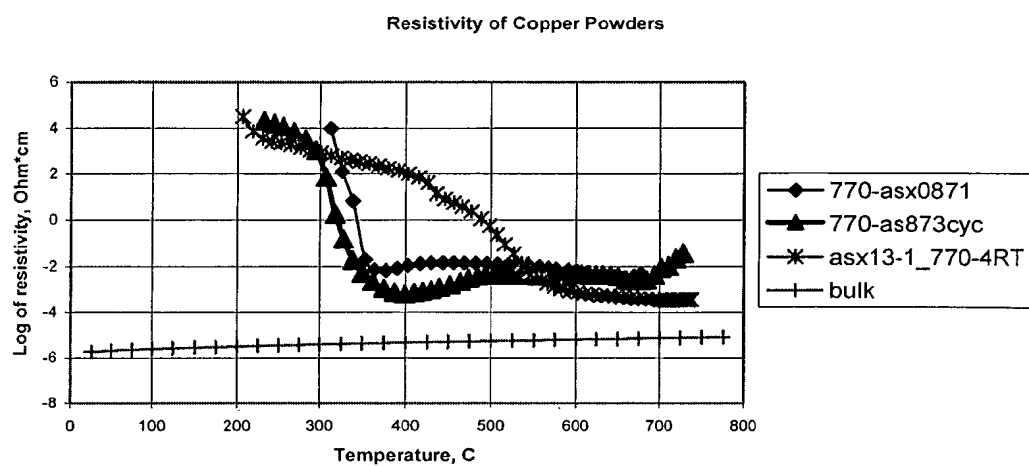


Figure 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 03/00554

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00 H05K1/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 379 745 B1 (JABLONSKI GREGORY A ET AL) 30 April 2002 (2002-04-30) claims 1-15; examples 5,6,10,12,13 column 14, line 52 -column 15, line 2 column 18, line 53 -column 19, line 15 ----	1,3-5, 14,15, 18,19, 21,23, 25-29
A	EP 0 977 212 A (IBM) 2 February 2000 (2000-02-02) claims 1-32 ----	1
A	WO 01 30520 A (LILLY CLIFFORD A JR ;CHRYSALIS TECHNOLOGIES INC (US); DEEVI SEETHA) 3 May 2001 (2001-05-03) -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 October 2003

Date of mailing of the international search report

05/11/2003

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